



Docket No.: 20441/0202715-US0
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Yasuyuki Goto et al.

Application No.: 10/543,036

Filed: July 21, 2005

For: ELECTROLUMINESCENCE DEVICE

Confirmation No.: 8433

Art Unit: 1774

Examiner: Dawn L. Garrett

DECLARATION UNDER 37 C.F.R. § 1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

We, Yasuyuki GOTO and Mitsuharu NOTO, being duly sworn, depose and say:

1. We are the co-inventors of the patent application identified above and we are the co-inventors of the subject matter described and claimed therein.

2. Prior to January 29, 2002, the effective date of the Seo et al. reference (U.S. Patent Application Publication No. 2002/0101154 A1 – hereinafter “Seo”), we conceived our invention as described and claimed in the subject application in this country, a NAFTA country, or a WTO member country.

3. Our invention was conceived in full, and due diligence was used to reduce it to practice, for example, by improving on further embodiments of the invention. As evidence that our work antedates Seo, we refer to: "Material for 011116 Study Group Meeting," attached hereto as Exhibit A, which is an English translation of a corresponding Japanese document, attached hereto as Exhibit C; and "Material for 001215 Study Group Meeting," attached hereto as Exhibit B, which is an English translation of a corresponding Japanese document, attached hereto as Exhibit D. These materials are in-house documents. We declare that these documents (Exhibits C and D) were created by us before January 29, 2002.
4. Claims 11-22 are rejected as anticipated by Seo in our application. The descriptions of Exhibits A and B support the subject matters of claims 11-18.
5. With respect to the subject matter of independent claim 11, both Exhibits A and B disclose a plurality of organic compound layers disposed between an anode and a cathode. Exhibit A discloses a layer of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine ("TPD"), a layer of 4,4-bis(carbazole-9-yl)-biphenyl ("CBP"), and a layer of 1,3-bis[5-(p-tert-butylphenyl)-1,3,4-oxadiazole-2-yl]benzene ("OXD-7"), all of which are organic compounds, disposed between an indium-tin-oxide ("ITO") anode and an aluminum ("Al") cathode. Exhibit A, page 1, lines 24-26. Exhibit B discloses a layer of TPD, a layer of CBP, a layer of bathocuproine ("BCP"), and a

layer of tris(8-hydroxyquinoline) aluminum (“alq”), all of which are organic compounds, disposed between an ITO anode and an aluminum-lithium (“AlLi”) cathode. Exhibit B, page 1, lines 27-31. In addition, both Exhibits A and B disclose an inorganic compound dispersed in one of the organic compound layers, thereby changing the luminescent color. Exhibit A discloses a CBP layer doped with EuBr₂ and further with CsI, accompanied by a change in the luminescent color. *See, e.g.*, Exhibit A, page 1, lines 32-34 (“As Fig. 1 shows, Eu²⁺ light emission having a peak at approximately 470 nm is observed in the low-current region. On the other hand, in the high-current region, sufficient energy transfer does not take place and CBP blue-light emission is observed.”). Exhibit B discloses a CBP layer doped with EuI₂, accompanied by a change in the luminescent color. *See, e.g.*, Exhibit B, page 1, line 39 (“Fig. 3 indicates that in element (1), CBP light emission remains.”). These descriptions support the subject matter of claim 11.

6. Claim 12 depends from claim 11. With respect to the additional subject matter of claim 12, both Exhibits A and B disclose that luminescence of the inorganic compound is achieved by a direct current voltage. For example, both Exhibits present plots of luminance (cd/m²) against current density (mA/cm²) (shown as the second figure of Exhibit C and the first figure of Exhibit D). These descriptions support the additional subject matter of claim 12.

7. Claims 13 and 14 depend from claims 11 and 12, respectively. With respect to the additional subject matter of claims 13 and 14, both Exhibits A and B disclose that a part of the inorganic compound is replaced to change the luminescent color. Exhibit A discloses replacing “3CBP:1EuBr₂” by “3CBP:0.5CsI:0.5EuBr₂,” accompanied by a change in the luminescent color. *See, e.g.*, Exhibit A, page 1, lines 35-36 (“It is believed that these [light emission characteristics] will be improved by optimizing the doping concentrations.”) and lines 39-41 (“The maximum luminance of the element [(1)] in this experiment was 183 cd/m² (current density 458 mA/cm², voltage 13 V). This was a significant improvement compared to the maximum luminance of 40 cd/m² of element (2).”). Exhibit B discloses replacing “1EuI₂:2CBP” by “1EuI₂:10CBP,” accompanied by a change in the luminescent color. *Compare, e.g.*, Figs. 2 and 3 of Exhibit B (shown as the second and third figures of Exhibit D). These descriptions support the additional subject matter of claims 13 and 14.

8. Claims 15, 16, 17, and 18 depend from claims 11, 12, 13, and 14, respectively. With respect to the additional subject matter of claims 15-18, both Exhibits A and B disclose that the inorganic compound is a metallic compound. Exhibit A discloses “CsI” and EuBr₂” and Exhibit B discloses “EuI₂.” Since it is well-known in the art that Cs and Eu are both metal atoms, these descriptions support the additional subject matter of claims 15-18.

9. We further declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: 9/22/2006

by Yasuyuki Goto
Yasuyuki GOTO, Co-Inventor

Dated: 9/22/2006

by Mitsuharu Noto
Mitsuharu NOTO, Co-Inventor

Material for 011116 Study Group Meeting

5

1. Objective

10 In our past research, we have found that it is possible to dope an organic semiconductor with a light-emitting inorganic salt and cause the inorganic salt to emit light. However, these light emissions were significantly different from the light-emission spectrum associated with the powder state and were a broad light emission strongly influenced by the crystal field (heptacoordinate Eu^{2+}).

15 We believed this to be due to insufficient crystal growth of the inorganic salt. Thus, this time we conducted an experiment with the aim of obtaining a sharp Eu^{2+} blue-light emission by doping the organic semiconductor CBP with the light-emitting inorganic salt EuBr_2 and further with CsI as a host material of the inorganic salt.

20

2. Experiment

The elements we prepared in this experiment are as follows.

25 (1) ITO/TPD(50nm)/3CBP:0.5CsI:0.5EuBr2(25nm)/OXD-7(50nm)/LiF/Al
(2) ITO/TPD(50nm)/3CBP:1EuBr2(25nm)/OXD-7(50nm)/LiF/Al

30

3. Experimental results and observations

35 Fig. 1 shows the light-emission spectra of the elements obtained in this experiment. As Fig. 1 shows, Eu^{2+} light emission having a peak at approximately 470 nm is observed in the low-current region. On the other hand, in the high-current region, sufficient energy transfer does not take place and CBP blue-light emission is observed. Also, in the long-wavelength region, broad light emission was observed. It is believed that these will be improved by optimizing the doping concentrations.

40 Fig. 2 shows the current-luminance characteristics of the element in this experiment. The maximum luminance of the element in this experiment was 183 cd/m² (current density 458 mA/cm², voltage 13 V). This was a significant improvement compared to the maximum luminance of 40 cd/m² of element (2).

Material for 001215 Study Group Meeting

5

I. Preparation of a hybrid EL element doped with EuI2

1. Objective

10

Recently, much attention has been given to organic EL elements that take advantage of light emission from the excited triplet state. However, aside from some organic compounds and heavy-metal complexes, light emission from the excited triplet state, i.e., phosphorescence, has almost never been observed at room temperature. Also, it has been stated as to these that light emission in the blue-light region at room temperature is difficult in view of its light-emission mechanism.

15

In this experiment, we used the inorganic salt EuI2, which emits light from both the sextet and octet spin states, to dope the representative organic EL host material CBP and studied its EL characteristics.

20

2. Experiment

25

We show the structures of the elements prepared in this experiment below.

30

1 ITO/TPD/ 1 EuI2:10CBP/BCP/alq/AlLi (1.3% (v/v) doping concentration when converted to standard organic matter)

35

2 ITO/TPD/ 1 EuI2: 2 CBP/BCP/alq/AlLi (7.0% (v/v) doping concentration when converted to standard organic matter)

3. Results and observations

35

Fig. 1 and Fig. 2 show the current-luminance characteristics and the EL spectrum of element (2). Also, Fig. 3 shows the EL spectrum of element (2).

40

Fig. 3 indicates that in element (1), CBP light emission remains. Also, it can be seen that the more current flows, the higher the peak on the long-wavelength side becomes. In general, the greater the exciton density, the stronger the excimer and exciplex peaks become. Thus, it can be seen that the peaks on the long-wavelength side are not peaks originating from exciplexes or excimers.

5 In element (1) (Fig. 2), only a peak that was completely on the long-wavelength side was observed. Spectrum of 850 nm or higher could not be measured due to limitations in the detecting equipment. Thus, a Gaussian peak was assumed, and since good consistency was found upon performing a fitting, extrapolation was carried out. As a result, it is estimated that the peak tail extends to around 1000 nm.

10 The maximum external quantum efficiency obtained from the spectrum and luminance was 0.18% (0.2 cd/m², 7.13 mA/cm²).

15 It is believed that further improvements in luminance and efficiency are possible by optimizing the host and doping concentrations.

20 On the other hand, with the PL in which CBP was doped with EuI₂, only weak fluorescence derived from CBP was observed, and the broad peak on the long-wavelength side that was observed with EL was not observed. Also, in the absorption spectrum, absorption derived from EuI₂ was observed as well (literature value 341 nm, measured value 347 nm). This indicated that EuI₂ doping was present.

25 Based on the above, it can be surmised that the light emission in the EL long-wavelength region is a phenomenon specific to EL and that this is taking place due to energy transfer from CBP. When light excitation of CBP is performed, almost no triplets are generated. On the other hand, in an EL, a triplet state is generated directly from the recombination of a positive hole and an electron. Thus, it is believed that EuI₂ emitted light due to energy transfer from the triplet state.

30 It has been reported that with Eu²⁺ in inorganic fluorescent bodies, combinations with different host materials result in shifts from purple to yellow. However, the peak value of the emitted light from this experiment is 687 nm.

35 It is necessary to investigate its assignment in the future.

[Figure captions]

35 Fig. 1. Current-luminance characteristics

40 Fig. 2. EL spectrum

[curve toward left] Standard luminosity curve

[curve toward right] Actual measurement

[rightmost segment in red] Gaussian fitting

Fig. 3. Current dependency of the EL spectrum of element (1)

Fig. 4. PL and the absorption spectra of thin films vapor-deposited on quartz substrate
[arrows] Stray light

011116 検討会資料

1. 目的

今までの研究において、我々は、有機半導体に発光性無機塩をドープし無機塩を発光させることができる事を明らかにした。しかしながら、これらの発光は、粉末状態の発光スペクトルとは著しく異なり、強く結晶場の影響をうけたプロードな発光（7配位 Eu^{2+} ）であった。

これは、無機塩が十分に結晶成長しなかったためと考えた。よって、今回、有機半導体CBPに発光性無機塩 EuBr_2 、さらに無機塩のホスト材料として CsI をドープしシャープな Eu^{2+} の青色発光を得ることを目的とし実験をおこなった。

2. 実験

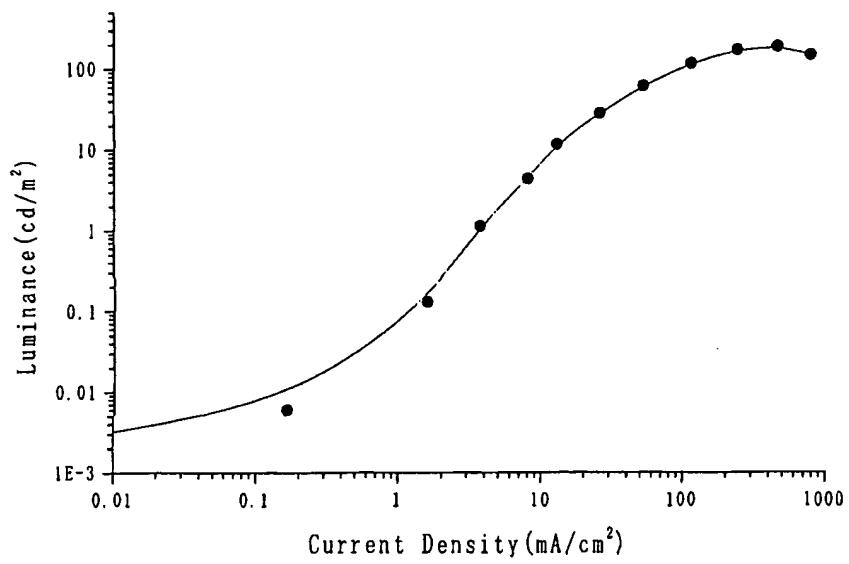
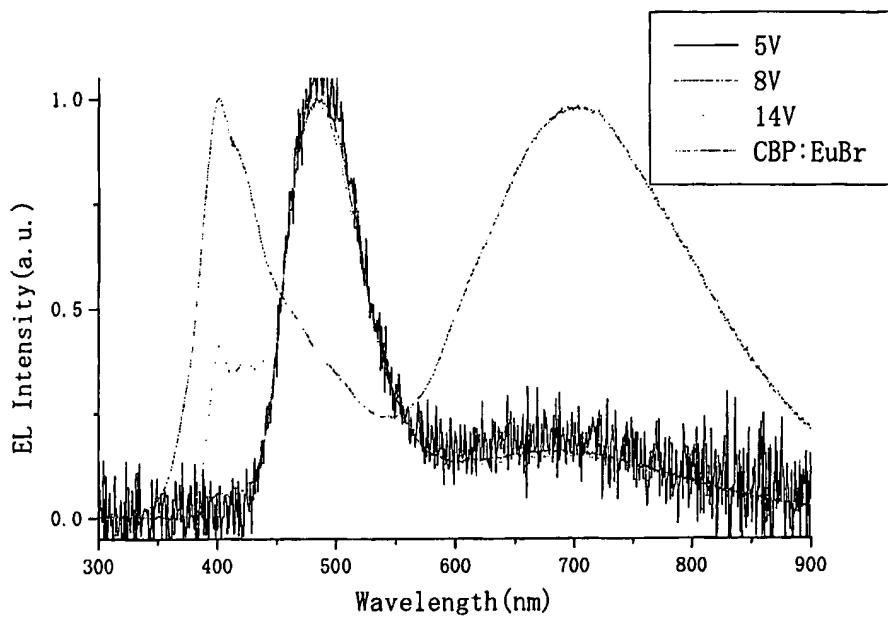
今回、作成した素子は以下の通りである。

- ① ITO/TPD(50nm)/3CBP:0.5CsI:0.5EuBr2(25nm)/OXD-7(50nm)/LiF/Al
- ② ITO/TPD(50nm)/3CBP:1EuBr2(25nm)/OXD-7(50nm)/LiF/Al

3. 実験結果及び考察

図1に今回得られた素子の発光スペクトルを示す。図1から分かるとおり低電流領域ではほぼ470nmにピークをもつ Eu^{2+} の発光が観察されている。一方、高電流領域ではエネルギー移動が十分に行われず、CBPの青色発光が観察されている。また、長波長領域には、プロードな発光が観察された。これらは、ドープ濃度の最適化で改善されると考えられる。

図2に今回の素子の電流-輝度特性を示す。今回の素子は最高輝度 $183\text{cd}/\text{m}^2$ （電流密度 $458\text{mA}/\text{cm}^2$ 、電圧 13 V）であった。これは、②素子の最高輝度 $40\text{cd}/\text{m}^2$ に比較し大幅に改善された。



001215 検討会資料

I. EuI2をドープしたハイブリッドEL素子の作製

1. 目的

近年、励起三重項状態からの発光を利用した有機EL素子が注目されている。しかし、ながら一部の有機化合物や重金属錯体をのぞいて励起三重項状態からの発光すなわち燐光は室温ではほとんど観察されない。また、それらは、その発光機構から青色領域の室温での発光は難しいと言われている。

今回、我々は、スピノ6重項及び8重項の両方から発光する無機塩EuI2を代表的な有機ELホスト材料CBPにドープしそのEL特性を調査した。

2. 実験

今回、作製した素子構造を以下に示す。

- 1 ITO/TPD/1 EuI2 : 10CBP/BCP/alq/AlLi (一般的な有機物に換算した場合のドープ濃度1.3% (v/v))
- 2 ITO/TPD/1 EuI2 : 2 CBP/BCP/alq/AlLi (一般的な有機物に換算した場合のドープ濃度7.0% (v/v))

3. 結果及び考察

図1及び図2に②素子の電流-輝度特性、及びELスペクトルを示す。また、図3に②素子のELスペクトルを示す。

図3より①素子ではCBPの発光が残っていることが分かる。また、電流が多く流れるほど長波長側のピークが高くなっていることが分かる。一般に励起子密度が上がるほどエキサイマー及びエキサイプレックスのピークは強くなる。よって、長波長側のピークはエキサイプレックス又はエキサイマーに由来するピークではないことが分かる。

素子①(図2)では、完全に長波長側のピークのみが観察された。検出器の限界で850nm以上のスペクトルは測定できなかったよってガウシアンピークと仮定しフィッティングを行った結果良い一致を示したので外挿した。その結果、ピークの裾は1000nm付近までのびていると推定される。

スペクトル及び輝度から最大外部量子効率を求めた結果、0.18%(0.2cd/m²、7.13mA/cm²)であった。

輝度及び効率は、ホスト及びドープ濃度の最適化でまだ改善は可能であると考えられる。一方、CBPにEuI2をドープしたPLではCBPに由来する弱い螢光しか観察されずELで観察された長波長側のブロードなピークは観察されなかった。また、吸収スペクトルでは

EuI₂に由来する吸収も観察された（文献値341nm、測定値347nm）。これより、EuI₂はドープされていることが分かった。

以上よりEL長波長領域の発光はEL特有の現象でありCBPからのエネルギー移動により起こっていることが推察される。CBPを光励起した場合、ほとんど三重項は生成しない。一方、ELでは正孔と電子の再結合により直接三重項状態が生成する。よって、三重項状態からのエネルギー移動によりEuI₂が発光したと考えられる。

無機の蛍光体におけるEu²⁺は、そのホスト材料との組み合わせで紫から黄色まではシフトすることが報告されている。しかしながら、今回の発光のピーク値は687nmである。

今後は、この帰属について検討する必要がある。

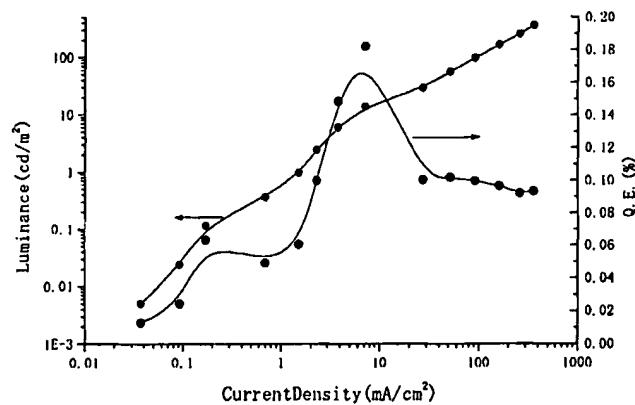


図1. 電流-輝度特性

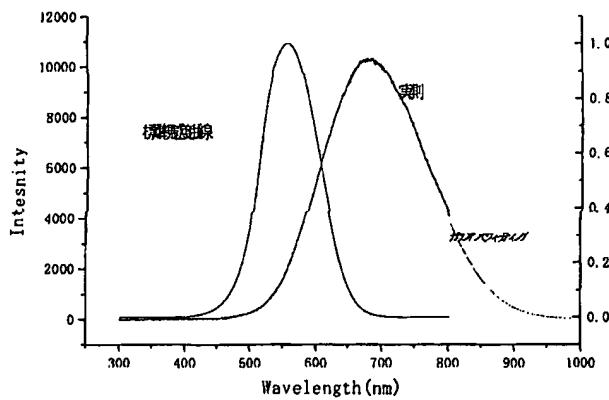


図2. ELスペクトル

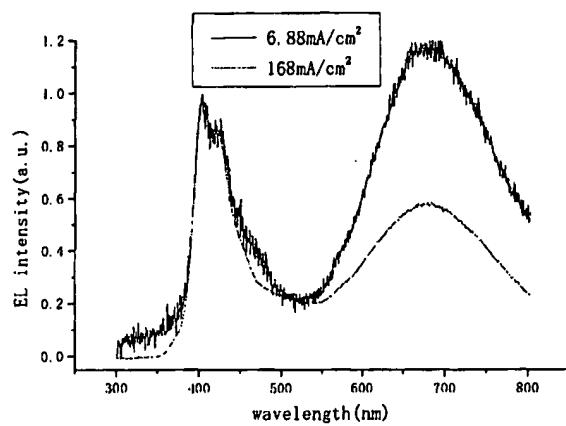


図3. 素子①のELスペクトルの電流依存性

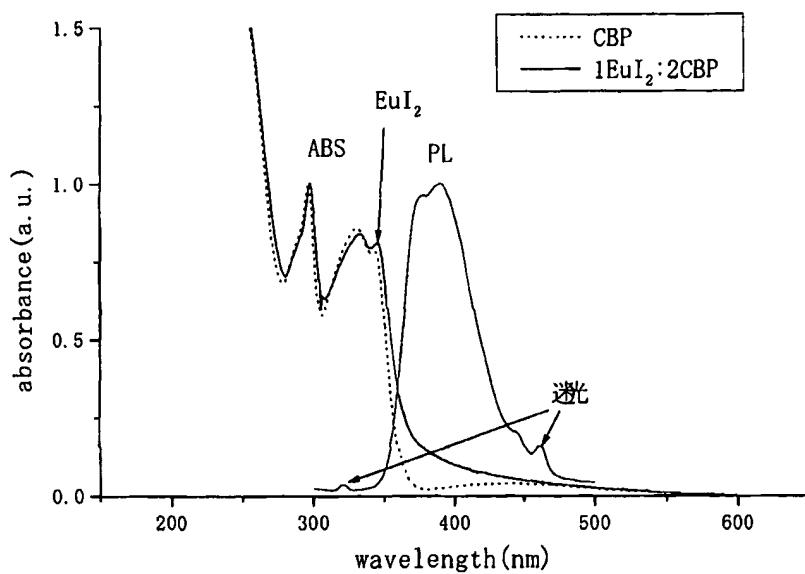


図4. 石英基板上に蒸着した薄膜のPL及び吸収スペクトル